CHARACTERIZATION OF THE RETINAL CHROMOPHORE IN THE GAS-PHASE VIA PHOTOISOMERIZATION ACTION SPECTROSCOPY

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The wavelength dependence for the photoisomerization of the isolated retinal protonated n-butylamine Schiff base (RPSB) is explored in the gas phase using a new technique that combines laser spectroscopy and ion mobility spectrometry. The technique involves exposing electrosprayed ions to tunable laser radiation as they are introduced into the drift region of an ion mobility spectrometer. Ions that absorb laser radiation photoisomerize, resulting in a detectable change in their drift speed through N_2 buffer gas. Without laser irradiation, 4 peaks are observed in the arrival time distribution of RPSB. The most intense and slowest peak is assigned as the all-*trans* isomer by comparison with the calculated collision cross sections. With laser radiation, there is a clear depletion of the all-*trans* isomer peak between 440 to 660 nm, corresponding to the $S_1 \leftarrow S_0$ transition, with a maximum effect at 615 ± 5 nm. There is also evidence of photoisomerization below 450 nm associated with the onset of the $S_2 \leftarrow S_0$ transition. The photoisomerization action spectrum of RPSB is expected to mimic its absorption spectrum and should prove useful for calibrating theoretical descriptions of the isolated chromophore.